TITLE

PREPARATION AND USE OF EXO-2-FLUOROALKYL(BICYCLO[2.2.1] HEPT-5-ENES

FIELD OF THE INVENTION

This invention relates to a monomer composition, a method for preparing the monomer composition and a polymer prepared therefrom. Polymers derived from the monomer composition are particularly suitable for use in a photoresist composition especially in the wavelength range shorter than 240 nm.

BACKGROUND OF THE INVENTION

In US 2002/0102490 of Ito et al., a process for synthesizing 3-(bicyclo[2.2.1]hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol by reaction of cyclopentadiene with 1,1,1 trifluoro-2-trifluoromethyl-4-penten-2-ol complex is described. The monomer mixture resulting from that synthesis has an endo/exo isomer ratio of 80/20. Ito et al. is silent on synthesizing 3-(bicyclo[2.2.1]hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol which is rich in the exo isomer. Ito et al. further discloses polymerizing 3-(bicyclo[2.2.1]hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol with fluorinated olefins.

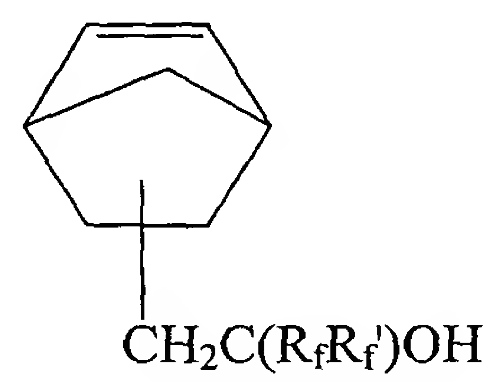
Ito et al in "Synthesis and evaluation of alicyclic backbone polymers for 193 nm lithography" ACS Symposium Series (1998), 706 Micro- and Nanopatterning Polymers 208-223, American Chemical Society, discloses that radical polymerization of 3-(bicyclo[2.2.1]hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol in the absence of catalyst is in general a very slow process thus to achieve reasonable addition polymerization rates of substituted norbornenes, metal based catalysts have been employed. Ito et al. identified certain comonomers, such as SO_2, which would increase the rate of polymerization. This very limited number of comonomers appear to enhance the rate of polymerization. However, the foregoing approaches have drawbacks. Metal based catalysts leave residues which are highly undesirable for use in short wavelength photolithographic applications; and, the use of comonomers, such as SO_2, degrade the transparency of the polymer at 157 nm. According to the Ito et al. publication the presence of SO_2 also decreases thermal stability of the polymer.

Polymers used in photoresist compositions must be highly transparent, highly free of contamination, particularly metallic contamination, must be processible according to the methods employed in

the art, and, of course, must be cost effective. Because of the potential for even minute metallic residues to contaminate nano-scale circuitry, it is highly desirable to prepare polymers for use in photoresist compositions without resort to metal catalysis.

SUMMARY OF THE INVENTION

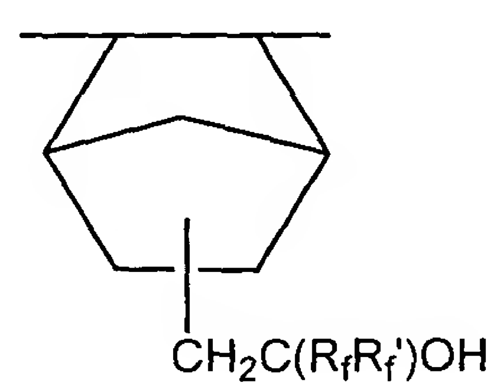
This invention relates to a composition comprising endo- and exo- 2-(bicyclo[2.2.1]hept-5-en-2-yl)- 2,2-fluoroalkyl-ethan-2-ol whereof the endo/exo concentration ratio is no greater than 5/95, as represented by the structure (I)



(I)

wherein the R_f and $R_{f'}$ groups are the same or different fluoroalkyl groups of from 1 to about 10 carbon atoms, or taken together in cyclic form are $(CF_2)_n$ where n is an integer from 2 to 10.

This invention also relates to a polymer comprising about 10 mol % to about 60 mole % of a repeat unit derived from a composition comprising endo and exo monomer units represented by structure (II)

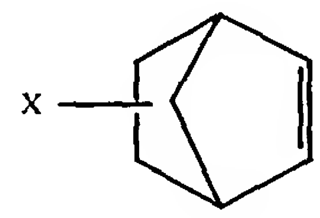


(II)

wherein the R_f and $R_{f'}$ groups are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms, or taken together in cyclic form are $(CF_2)_n$; n is an integer from 2 to 10; the monomer units of the composition having an endo/exo ratio no greater than 5/95.

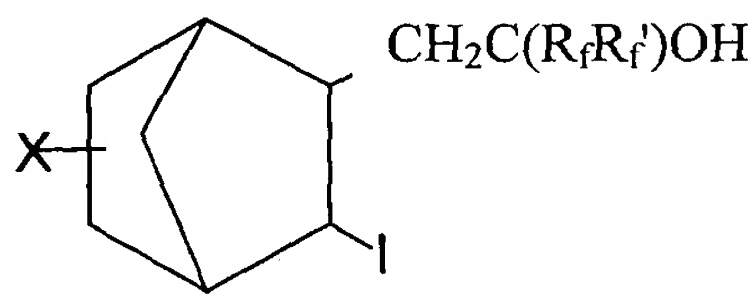
This invention still further relates to a process for preparing a composition comprising endo- and exo- 2-bicyclo[2.2.1]hept-5-en-2-yl)- 2,2-fluoroalkyl-ethan-2-ol whereof the endo/exo concentration ratio is no greater than about 5/95, the process, comprising the steps of:

contacting in the presence of a source of free radicals a substituted norbornene with $ICH_2C(R_f)(R_f')OH$; wherein said substituted norbornene is represented by the structure (III)



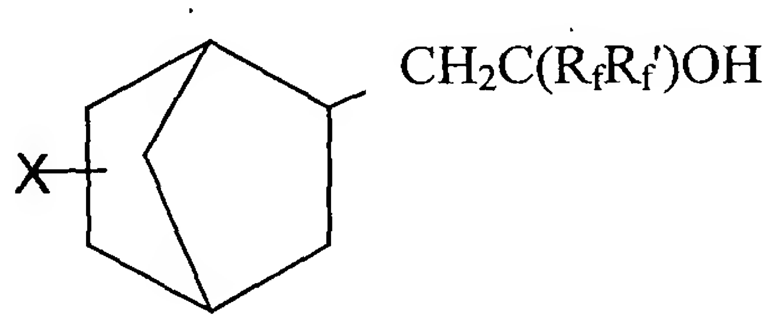
(III)

to form an iodine-containing substituted norbornane compound represented by structure (IV);



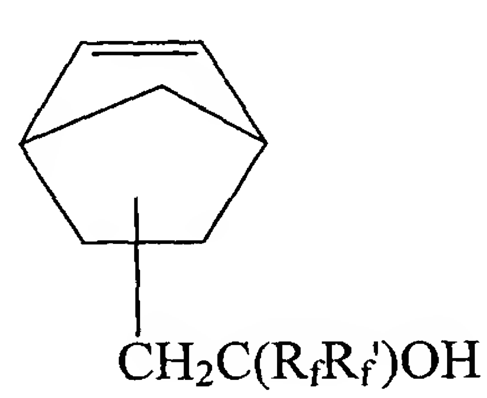
(IV)

contacting said iodine-containing compound with a reducing agent to form a substituted norbornane represented by structure (V);



V

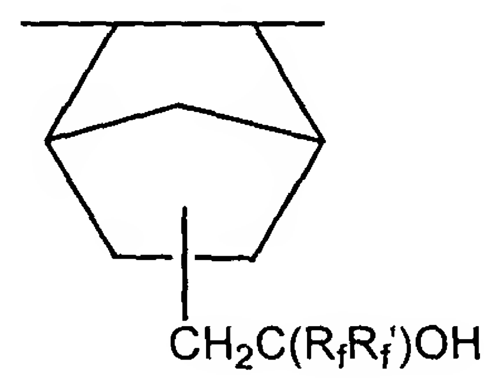
forming an olefin from the substituted norbornane (V) to form a composition comprising endo and exo 2-(bicyclo[2.2.1]hept-5-en-2-yl)- 2,2-perfluoroalkyl-ethan-2-ol, whereof the endo/exo concentration ratio is no greater than 5/95 as represented by the structure (I).



(I)

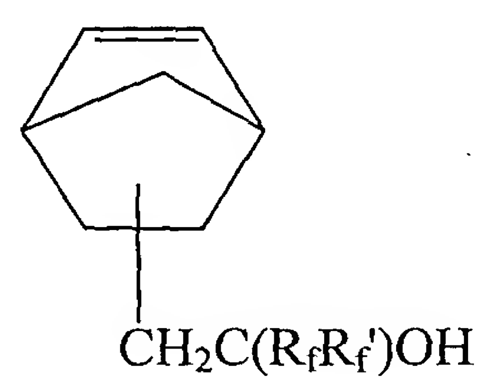
wherein in the foregoing structures the R_f and $R_{f'}$ groups are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms, or taken together in cyclic form are $(CF_2)_n$, n is an integer from 2 to 10, and wherein X is selected from the group consisting of Cl, Br, and R_8SO_2—O—, where R_8 is an alkyl-, fluoroalkyl, aryl or fluoroaryl radical.

A photoresist suitable for use in the preparation of electronic circuits said photoresist comprising a photoactive agent and a polymer compromising 10 mol-% to 60 mol-% of A repeat unit represented by the structure (II)



(II)

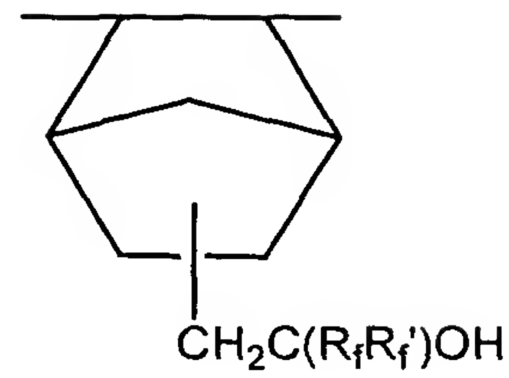
and whereof said repeat unit is derived from a composition comprising endo- and exo- 2-(bicyclo[2.2.1]hept-5-en-2-yl)- 2,2-fluoroalkyl-ethan-2-ol, as represented by the structure (I)



(I)

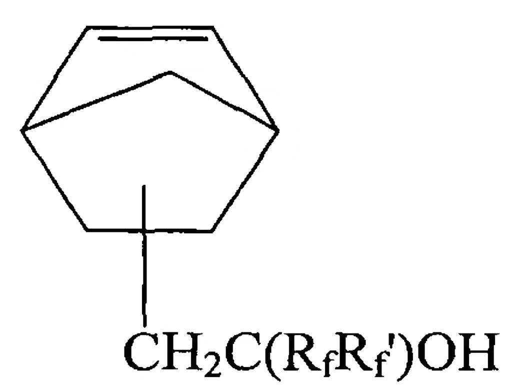
wherein the R_f and $R_{f'}$ groups are the same or different fluoroalkyl groups of from 1 to about 10 carbon atoms, or taken together in cyclic form are $(CF_2)_n$ where n is an integer from 2 to 10, whereof the endo/exo ratio is no greater than 5/95.

In a yet further aspect, this invention relates to an article comprising a semiconducting substrate having a surface, and a photoresist film disposed upon at least a portion of said surface, said photoresist film comprising a photoactive agent and a polymer compromising 10 mol-% to 60 mol-% of a repeat unit represented by the structure (II)



(II)

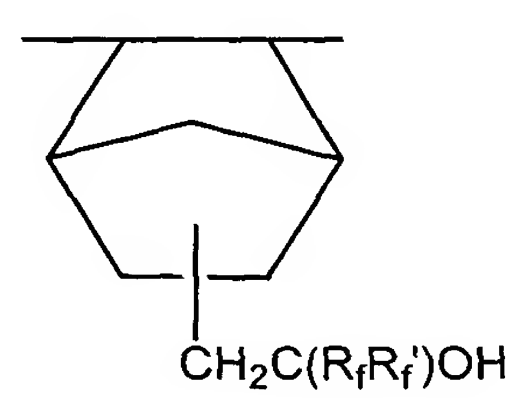
and whereof said repeat unit is derived from a composition comprising endo- and exo- 2-(bicyclo[2.2.1]hept-5-en-2-yl)- 2,2-fluoroalkyl-ethan-2-ol, as represented by the structure (I)



(I)

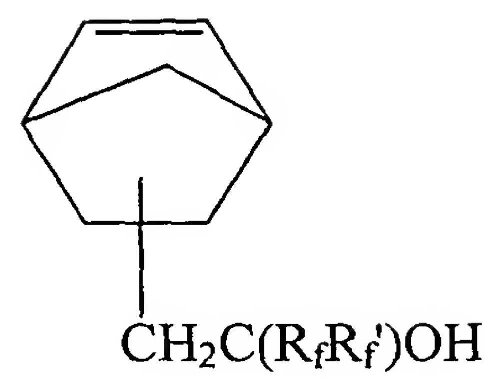
wherein the R_f and $R_{f'}$ groups are the same or different fluoroalkyl groups of from 1 to about 10 carbon atoms, or taken together in cyclic form are $(CF_2)_n$ where n is an integer from 2 to 10, whereof the endo/exo ratio is no greater than 5/95.

A process for preparing a patterned article the process comprising: forming a target surface by disposing upon a semiconducting substrate a photoresist film comprising a photoactive agent and a polymer compromising 10 mol-% to 60 mol-% of repeat units represented by the structure (II)



(II)

whereof said repeat units are derived from a composition comprising endo- and exo- 2-(bicyclo[2.2.1]hept-5-en-2-yl)- 2,2-fluoroalkyl-ethan-2-ol, as represented by the structure (I)



(I)

wherein the R_f and $R_{f'}$ groups are the same or different fluoroalkyl groups of from 1 to about 10 carbon atoms, or taken together in cyclic form are $(CF_2)_n$ where n is an integer from 2 to 10, whereof the endo/exo ratio is no greater than 5/95; illuminating said target surface in such a manner as to form a pattern of shadowed and illuminated areas, the illuminating step causing a change in solubility of said polymer; removing the soluble portions of said polymer, thereby producing a patterned article.

DETAILED DISCUSSION OF THE INVENTION

The present invention is directed to a composition of exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)- 2,2-fluoroalkyl-ethan-2-ol, a method for preparing said composition, a polymer comprising repeat units derived from said composition and methods of synthesizing such composition.

The invention relates to a composition of 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol with a high preponderance of the exo isomer. The as-synthesized composition is rich in exo isomer. A high preponderance of exo isomer is typically no greater than an endo/exo concentration of about 5/95, preferably no greater than 5/95.

The invention also relates to the discovery that the exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol of the invention copolymerizes by free-radical addition to higher yield than does a composition containing an 80/20 endo/exo ratio. The free radical addition polymerization is preferably conducted in the absence of metal catalyst. In particular, a copolymer of exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol with a halogenated, preferably fluorinated, α-unsaturated olefinic comonomer, preferably tetrafluoroethylene, is formed in higher yields than the 80/20 endo/exo mixture. Free-radical addition, in the absence of a metal catalyst, of a composition comprising exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol can achieve a three-fold yield increase.

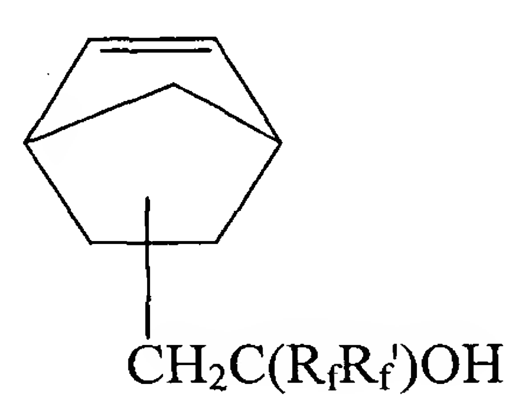
Further, polymers derived from the exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol are characterized by surprisingly high

incorporation of repeat units derived from the 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol monomer.

Polymers derived from the exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol also have very high transparency. Because of its transparency properties the polymer can be useful in a variety of optical applications such as photoresists, optical waveguides, optical elements such as lenses, pellicles, beam splitters, diffraction gratings, or optical couplets.

Thus, in one embodiment, the invention relates to a photoresist composition comprising a polymer derived from 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol, an article comprising a semiconducting substrate with a photoresist comprising a polymer derived from 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol disposed upon at least a portion thereof and processes for preparing the article and patterning the article.

In one embodiment of the invention there is provided a substituted norbornene composition comprising a mixture of endo- and exo- 1-(bicyclo[2.2.1]hept-5-en-2-yl)- 2,2-fluoroalkyl-ethan-2-ol whereof the endo/exo concentration ratio is no greater than 5/95. The 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol, is represented by the structure (I)

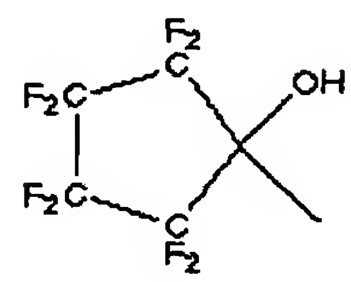


(I)

wherein the R_f and $R_{f'}$ groups are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms, or taken together in cyclic form are $(CF_2)_n$ where n is an integer from 2 to 10. Either or both of R_f and R_f' can be partially fluorinated alkyl groups or fully fluorinated alkyl groups (i.e., perfluoroalkyl groups). Preferably R_f and $R_{f'}$ are perfluoromethyl or perfluoroethyl. Most preferably, R_f and $R_{f'}$ are perfluoromethyl.

For purposes of the present invention the term "taken together in cyclic form" means that the R_f and $R_{f'}$ groups are not separate, discrete fluorinated alkyl groups, but that together they form a ring structure. One

embodiment of such ring structure is illustrated by, but not limited to, the 5-membered ring:

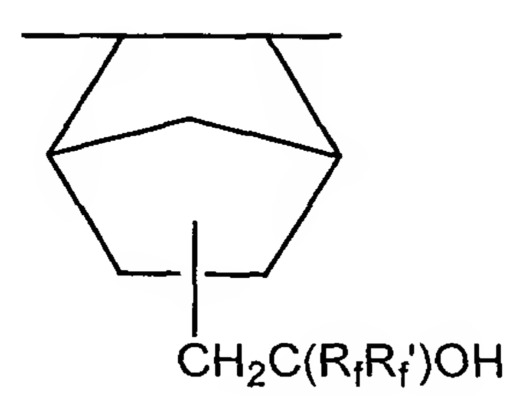


One of skill in the art will appreciate that numerous other embodiments of ring structures are also encompassed in the present invention.

In one embodiment of the invention, the exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol composition can be polymerized in the absence of a different comonomer in the presence of a metal catalyst.

Alternatively, the exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol composition can be polymerized with one or more different monomers, preferably by free radical addition which avoids the need for metal catalysts.

In a further embodiment of the present invention a polymer can comprise 10 mol-% to 60 mol-% of repeat units represented by the structure (II)



(II)

wherein the R_f and $R_{f'}$ groups are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms typically 1 to 5 carbon atoms, or taken together in cyclic form are $(CF_2)_n$ where n is an integer from 2 to 10, the polymer being derived from exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol. Preferably R_f is perfluoromethyl or perfluoroethyl. Most preferably R_f is perfluoromethyl. The polymer can contain up to about 90 mol-%, preferably about 40 to about 90% of units derived from one or more different monomers.

Different monomers that can be incorporated into the polymer can be derived from one or more olefins which may contain one or more

heteroatoms. Typically such olefins contain from about 2 to about 20 carbon atoms. Suitable heteroatoms include, without limit, halogen atoms, oxygen atoms, and nitrogen atoms. The olefin may be straight chain or branched chain and may contain one or more single-ring or multi-ring saturated or unsaturated hydrocarbon groups which may also contain one or more heteroatom substituents such as oxygen, halogen, and nitrogen. When the monomer comprises a single ring or multi ring group such cyclic group can contain from 3 to 18 carbon atoms. Examples of cyclic groups include norbornyl, adamantyl, 2-methyl-2-adamantyl, isobornyl and the like. When the monomer comprises a heteroatom it may contain one or more halogen atoms, carboxylic groups, hydroxyl groups, ester groups, carbonyl groups and carboxyl groups, ether groups, amide groups and nitrile groups.

In one embodiment of the invention the polymer is derived from the monomer represented by structure (I) and at least one halogenated olefin, specifically, a fluoroolefin having at least one fluorine atom attached to an ethylenically unsaturated carbon. The fluoroolefin can comprise from 2 to about 20 carbon atoms. Preferred fluoroolefins include tetrafluoroethylene, hexafluoropropylene, chlorotrifluoroethylene, vinylidene fluoride, vinyl fluoride, perfluoro-(2,2-dimethyl-1,3-dioxole), perfluoro-(2-methylene-4-methyl-1,3-dioxolane), $CF_2{=}CFO(CF_2)_tCF{=}CF_2$, where t is 1 or 2, and $R_f''OCF{=}CF_2$ wherein R_f'' is a fluoroalkyl group of from 1 to about 10 carbon atoms. Most preferred is tetrafluoroethylene.

The polymer can further comprise one or more units which provide useful functionality in photolithographic applications. Such functionality is imparted by chemical groups that promote or facilitate adhesion to the substrate, etch resistance, developability, high contrast, high process latitude, and low line edge roughness.

In one embodiment of this invention, the polymer contains one or more protected acidic groups that yield a carboxylic acid as the hydrophilic group upon exposure to photogenerated acid. Such protected acidic groups include, but are not limited to, A) esters capable of forming, or rearranging to, a tertiary cation, B) esters of lactone, C) acetal esters, D) β-cyclic ketone esters, E) α-cyclic ether esters, and F) MEEMA (methoxy ethoxy ethyl methacrylate) and other esters which are easily hydrolyzable because of anchimeric assistance. Some specific examples in category A) are t-butyl ester, 2-methyl-2-adamantyl ester, and isobornyl ester.

Polymer derived from the exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol preferably comprise one or more components having protected acidic fluorinated alcohol groups (e.g., $-C(R_f)(R_f')OR_a$, where R_a is not H) and/or other acidic groups that can yield hydrophilic groups by the reaction with acids or bases generated photolytically such as from photoactive compounds (PACs). A protected fluorinated alcohol group contains a group that protects the fluorinated alcohol group from exhibiting its acidity while in this protected form. A protecting group (R_a) is normally chosen on the basis of its being acid-labile, such that when acid is produced upon imagewise exposure, it will catalyze deprotection of the protected acidic fluorinated alcohol groups and/or other protected acidic groups and production of hydrophilic acidic groups that are necessary for development under aqueous conditions. In addition, the fluorine-containing copolymers may also contain acid functionality that is not protected (e.g., $-C(R_f)(R_f')OR_a$, where $R_a = H$).

As one illustrative example, when the tertiary-butyl group is the protecting group in a tertiary-butyl ester and this protecting group protects the free acid. In undergoing deprotection (conversion of protected acid to free acid), the ester is converted to the corresponding acid.

An alpha-alkoxyalkyl ether group (i.e., $R_a = OR_b$, $R_b = C_1\text{-}C_{11}$ alkyl) is a preferred protecting group for the fluoroalcohol group because it has been found to provide a high degree of transparency in the photoresist composition. An illustrative, but non-limiting, example of an alpha-alkoxyalkyl ether group that is effective as a protecting group, is methoxy methyl ether (MOM). A protected fluoroalcohol with this particular protecting group can be obtained by reaction of chloromethylmethyl ether with the fluoroalcohol. An especially preferred protected fluoroalcohol group has the structure:

$$-C(R_f)(R_f')O-CH_2OCH_2R_1$$

wherein, R_f and R_f' are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms or taken together in cyclic form $(CF_2)_n$ wherein n is 2 to 10; R_1 is H, a linear alkyl group of 1 to 10 carbon atoms, or a branched alkyl group of 3 to 10 carbon atoms.

The fluoroalcohol functional group (protected or unprotected) of this invention can be used alone or it can be used in combination with one or more other acidic groups, such as carboxylic acid functional group

(unprotected) and t-butyl ester of carboxylic acid functional group (protected).

Carbonates formed from a fluorinated alcohol and a tertiary aliphatic alcohol can also be used as protected acidic fluorinated alcohol groups.

In one embodiment of the invention the polymer comprises a hydroxy ester group which serves as a protected acidic group. An example of a hydroxy ester group which may be incorporated into the polymer of this invention has the formula

$$-CO_2-C(R^2)(R^3)-[C(R^4)(R^5)]_m-C(R^6)(R^7)-OH,$$

wherein

$m = 0, 1, 2, 3, 4$ or 5;

$R^2, R^3 = C_1 - C_6$ alkyl, $C_1 - C_6$ alkyl substituted with an ether oxygen; or R^2 and R^3 taken together form a 3- to 8-membered ring, optionally substituted with an ether oxygen, provided that the carbon attached to R^2 and R^3 is not at a bridgehead position;

$R^4, R^5 = H, C_1 - C_6$ alkyl, $C_1 - C_6$ alkyl substituted with an ether oxygen; or R^4 and R^5 taken together form a 3- to 8-membered ring, optionally substituted with an ether oxygen;

$R^6, R^7 = H, C_1 - C_6$ alkyl, or $C_1 - C_6$ alkyl substituted with an ether oxygen; or R^6 and R^7 taken together form a 3- to 8-membered ring, optionally substituted with an ether oxygen; or R^2 and R^6 taken together with $-[C(R^4)(R^5)]_{m1}-$ form a 4- to 8-membered ring, provided that the carbon attached to R^2 and R^3 is not at a bridgehead position.

In a preferred embodiment of this invention,

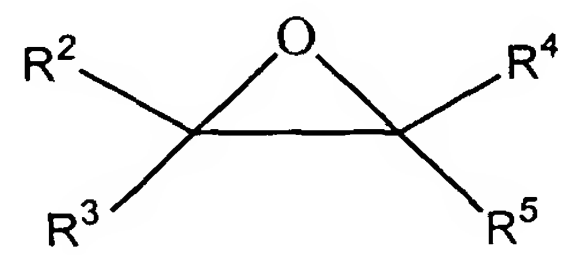
$R^2, R^3 = C_1$-C_6 alkyl, or R^2 and R^3 taken together form a 5- or 6-membered ring, provided that the carbon attached to R^1 and R^2 is not at a bridgehead position;

$R^4, R^5 = H, C_1 - C_6$ alkyl, or R^4 and R^5 taken together form a 5- or 6-membered ring;

$R^6, R^7 = H, C_1 - C_6$ alkyl, or R^6 and R^7 taken together form a 5- or 6-membered ring; and

$m_1 = 0, 1, 2$ or 3.

The hydroxy ester group of the formula $-CO_2-C(R^2)(R^3)-[C(R^4)(R^5)]_m-C(R^6)(R^7)-OH$ can be incorporated into polymers and copolymers by any of the several methods known to those skilled in the art. For example, acid-functionalized polymers can be reacted with a diol, $HO-C(R^2)(R^3)-[C(R^4)(R^5)]_m-C(R^6)(R^7)-OH$ or an epoxide



wherein R_2-R_7 are defined above to give the corresponding ester.

The hydroxy ester group of the present invention can be incorporated into an ethylenically unsaturated compound that is polymerized with other monomers, to form the desired hydroxy ester functionalized polymer. For example, the acrylate, $H_2C=C(H)CO_2-C(R^2)(R^3)-[C(R^4)(R^5)]_m-C(R^6)(R^7)-OH$, can be copolymerized.

Suitable hydroxy esters include 2-propenoic acid, 2-hydroxy-1,1,2-trimethylpropyl ester (PinAc) and the analogous methacrylate monomer (PinMAc), and the mono-acrylate and mono-methacrylate derivatives of 2,5-dimethyl-2,5-hexanediol. Suitable hydroxy esters can also be prepared from the products of the reductive dimerization of a wide variety of aliphatic and cycloaliphatic ketones, such a cyclohexanone, cyclopentanone and methyl ethyl ketone. Suitable hydroxy esters and the method of synthesizing them are described in U.S. Provisional Application No. 60/415,855 filed on October 3, 2002 which is incorporated herein by reference in its entirety.

In one embodiment, the polymer can comprise other esters. Acrylate comonomers that can be polymerized with the exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol include acrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, tert-butyl acrylate, 2-methyl-2-adamantyl acrylate, 2-methyl-2-norbornyl acrylate, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, 2-cyanoethyl acrylate, glycidyl acrylate, and 2,2,2-trifluoroethyl acrylate, as well as the corresponding methacrylate monomers. Such acrylates, as well as methacrylates, can be polymerized together with the exo-rich 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2,2-fluoroalkyl-ethan-2-ol and along with other ethylenically unsaturated compounds such as other fluoro-olefins and/or other polycyclic olefins.

In this invention, often, but not always, the components having protected groups are repeat units that have been incorporated in a copolymer that forms a component of a composition (as discussed above). Frequently the protected acidic groups are present in one or more comonomers that are polymerized to form a given copolymer of this invention. Alternatively, in this invention, a copolymer can be formed by copolymerization with an acid-containing comonomer and then subsequently acid functionality in the resulting acid-containing copolymer can be partially or wholly converted by appropriate means to derivatives having protected acidic groups.

In a still further embodiment, the polymer can be a tetrapolymer formed by uniting four different monomers and each monomer, typically imparts a different functionality (adhesion to the substrate, etch resistance, developability) such that the tetrapolymer encompasses more than one functionality.

In a preferred embodiment, the invention comprises a terpolymer derived from the exo-rich 1-(bicyclop2.2.1]hept-5-en-2-yl)-2,2-fluroalkyl-ethan-z-ol composition, an olefinic monomer having at least one fluorine atom attached to an olefinic carbon atom, and a tertiary alkyl acrylate. The tertiary alkyl acrylate provides protected acidic groups in the polymer which, when subjected to photogenerated acid, are converted to hydrophilic acidic groups for development of a resist coating.

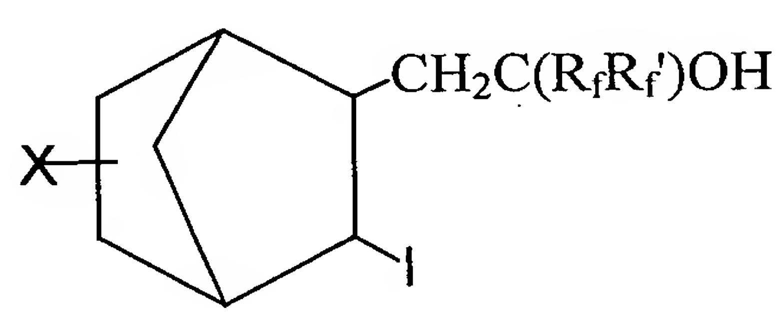
In a first step of the process of the invention for making the exo-rich monomer composition, in the presence of a source of free radicals, an iodine substituted fluoroalcohol such as $ICH_2C(R_f)(R_{f'})OH$ where R_f and $R_{f'}$ is defined above, is contacted with a substituted norbornene represented by the structure (III) hereinabove where X may be attached to either adjacent secondary carbons and X is a leaving group selected from the group consisting of Cl, F, Br, R_8SO_2—O—, wherein R_8 is an alkyl, fluoroalkyl aryl or fluoroaryl radical. Typically, the alkyl group contains from 1 to 20 carbon atoms and the aryl group contains from 3 to 20 carbon atoms. Preferably X is Cl and R_f and $R_{f'}$ is perfluoromethyl. A suitable reaction temperature is employed which is typically above ambient (20-25°C), more typically from about 50 to about 90°C.

$ICH_2C(R_fR_f')OH$ wherein R_f and R_f' are defined above, preferably $ICH_2C(CF_3)_2OH$, can be prepared by reaction of 47% hydroiodic acid with 2,2-bis(fluoroalkyl)oxirane, preferably 2,2-bis(trifluoromethyl)oxirane (for

when R_f and $R_{f'}$ is perfluoromethyl), according to the method of V.A.Petrov, *Synthesis*, No, 15, 2225, 2002.

In one embodiment, a mixture of endo and exo isomers of 5-chloronorbornene-2 is prepared by Diels-Alder reaction of vinyl chloride and dicyclopentadiene. Such a reaction is typically conducted at elevated temperatures. A reaction temperature of about 180°C for a reaction time of about 12 hours was reported in Roberts et al, *J. American Chem. Soc.*, 72 (1950), 3116. The product of this reaction is a mixture of exo and endo isomers but is predominantly endo, typically 80% endo.

In a more preferred embodiment of the process of the invention, exo-5-chloronorbornene-2 is prepared by low temperature addition of HCl to norbornadiene according to the method of L. Schmerling, J.P. Luvisi, W. Welch, *JACS*, 78, 2819. It is found surprisingly in the practice of the invention that when the exo-5-chloronorbornene is employed in preference to the endo/exo mixture, the addition reaction of $ICH_2C(CF_3)_2OH$ to the double bond of the composition represented by structure (III), wherein X = chlorine, produces a higher yield of the composition represented by the structure (IV)



(IV)

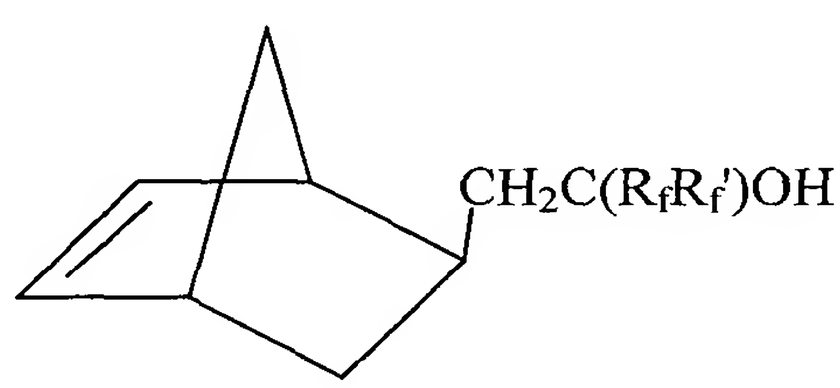
In the next step, the C—I bond is reduced to a C—H bond. Any method by which this can be accomplished is suitable. Suitable methods include but are not limited to Zn reduction as described in Brace, *J. Org. Chem.* 27 (1962), 3027 ff and, catalytic reduction with a palladium catalyst as described in Brace, *J. Fluorine Chem.* **20** (1982) 313ff. More broadly, catalytic hydrogenolysis is also described in Augstine, Catalytic Hydrogenolysis, Marcel Dekker, New York (1965), 125-146.

Metal reduction of compounds represented by structure IV can be carried out using metals, such as Zn, Zn/Cu, or Fe in a suitable solvent at elevated temperatures, typically from about 30 to about 100°C, in the presence of one or more acids such as for example, hydroiodic, hydrobromic or hydrochloric.

Reduction of compounds represented by structure IV using hydrogen can also be carried out. An inert solvent is used, typically an

aqueous solvent or an organic solvent (such as one or more of an alcohol, tetrahydrofuran, a glyme, etc.) in the presence of a hydrogenation catalyst (for example a Pd or Pt catalyst) and suitable base (sodium and potassium bicarbonates or carbonates, amines and the like) at an elevated temperature typically ranging from about 40 to about 100°C, preferably about 45 to about 100°C. The method based on use of hydrogen is preferred one, since that method avoids the formation of by- products. Hydrogen reduction is preferred when the exo-chloride is used, but either method is suitable when the endo/exo chloride is used.

Formation of olefins by elimination of HCl from an alkyl chloride is a known reaction, and may be conducted but is not limited to, according to the method of Bartsch et al, *J. Org. Chem.* 56, 212 (1991) using suitable strong base, such as potassium t-butoxide in solvents such as for example THF, diglyme or triglyme. In a preferred embodiment of the invention, the resulting product is a composition comprising a mixture of endo- and exo-2-(bicyclo[2.2.1]hept-5-en-2-yl)- 2,2-perfluoroalkyl-ethan-2-ol whereof the endo/exo concentration ratio is no greater than 5/95, whereof the exo portion is represented by the structure (VI)



VI

wherein the R_f and $R_{f'}$ groups are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms, or taken together in cyclic form are $(CF_2)_n$ where n is an integer from 2 to 10, preferably perfluoromethyl or perfluoroethyl, most preferably perfluoromethyl.

The olefinically unsaturated composition represented by structure (I) or in a preferred embodiment, the olefinically unsaturated composition represented by structure (VI), wherein R_f and $R_{f'}$ is trifluoromethyl, may be contacted with a source of free radicals in the presence of a fluoroolefin and caused to polymerize to form the polymer of the invention comprising repeat units represented by the structure (II). Suitable sources of free radicals included peroxy compounds, such as bis(4-tert-butylcyclohexyl)peroxydicarbonate and $CF_3CF_2CF_2OCF(CF_3)CO_2O_2CCF(CF_3)OCF_2CF_2CF_3$, and azo

compounds, such as azo-bis-isobutyronitrile. Polymerization temperatures are generally selected in accord with the half-life of the free radical source and are typically in the range of about 0°C to about 200°C, more preferably in the range of about 40°C to about 100°C.

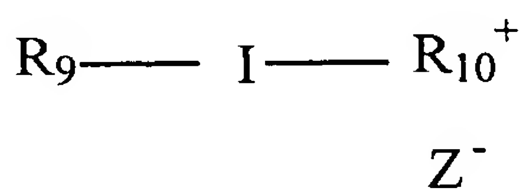
Polymerizations are preferably conducted in a closed reaction vessel to minimize loss of volatile reagents and in the absence of oxygen. Polymerizations may be conducted without solvent when the mixture of monomers forms a liquid phase or in the presence of solvent. Solvents are generally chosen to avoid undesirable chain transfer during the course of polymerization. Suitable solvents include chlorofluorocarbons, such as 1,1,1-trichlorotrifluoroethane, hydrofluorocarbons, such as 1,1,1,3,3-pentafluorobutane, esters, such as methyl acetate and ethyl acetate, and tertiary alkyl alcohols, such as tert-butanol.

Polymerizations may be conducted in a batch mode, that is, all reagents are added to the reaction vessel which is then heated to the desired polymerization temperature. More preferably, polymerizations may be conducted in a semi-batch mode in which portions of the monomers and solvent are added to the reaction vessel and are brought to polymerization temperature. The remaining monomers, solvent and free radical source are then fed to the reaction vessel so as to cause polymerization. A continuous process may also be employed in which monomers, solvent and free radical source are fed to a reaction vessel and a reactor stream containing the desired product is removed throughout the process.

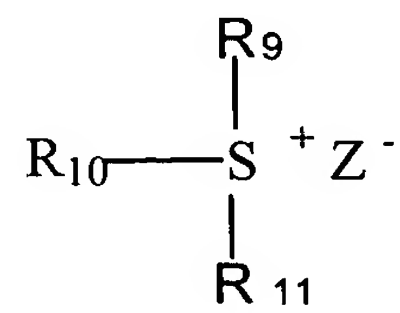
Preferably the exo-rich monomer composition of this invention is used in the polymerization; however, a monomer composition with a reduced exo content may be employed by adding to the polymerization feed a conventional higher endo content composition such as the kind described in US 2002/0102490 of Ito et al.

The polymers of this invention can be used as the binder of a photoresist composition by combining one or more polymers described herein with at least one photoactive component (PAC) such as are well-known in the art. A PAC is a compound that typically affords either acid or base upon exposure to actinic radiation. If an acid is produced upon exposure to actinic radiation, the PAC is termed a photoacid generator (PAG). If a base is produced upon exposure to actinic radiation, the PAC is termed a photobase generator (PBG). Several suitable photoacid generators are disclosed in WO 00/66575.

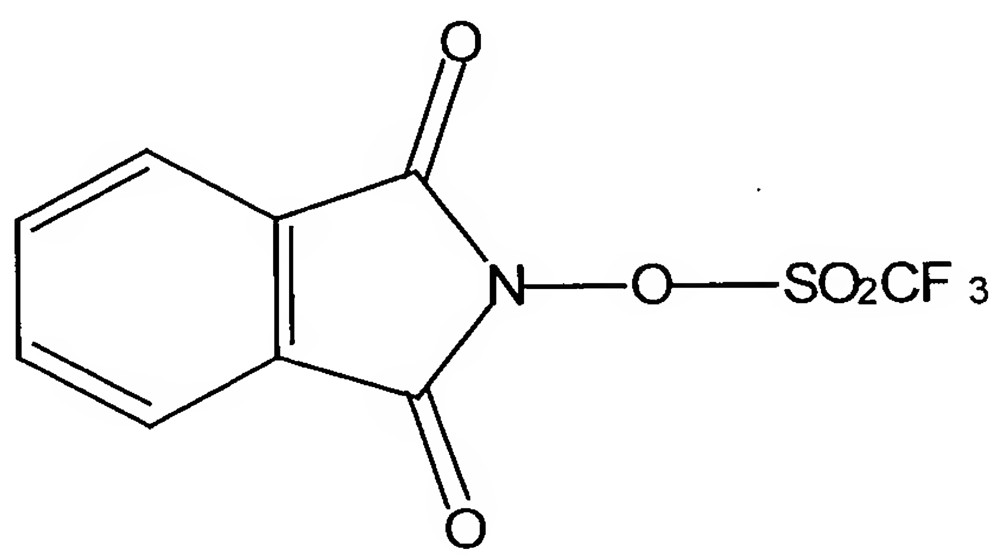
A PAG (photoacid generator) is a preferred subset of PAC (photoactive components). Suitable photoacid generators for this invention include, but are not limited to, 1) sulfonium salts (structure XI), 2) iodonium salts (structure XII), and 3) hydroxamic acid esters, such as structure XIII.



XII



XI



XIII

In structures XI and XII, R_9-R_{11} are independently substituted or unsubstituted C_6-C_{20} aryl or substituted or unsubstituted C_7-C_{40} alkylaryl or aralkyl. Representative aryl groups include, but are not limited to, phenyl, naphthyl and anthracenyl. Suitable substituents include, but are not limited to, one or more oxygen, nitrogen, halogen, or sulfur atoms. When the heteroatom is oxygen the substituent can contain hydroxyl (-OH) and C_1-C_{20} alkyloxy (e.g., $C_{10}H_{21}O$. The anion Z- in structures I-II can be, but is not limited to, SbF_6- (hexafluoroantimonate), CF_3SO_3- (trifluoromethylsulfonate = triflate), and $C_4F_9SO_3$- (perfluorobutylsulfonate). A typical PAG is triphenylsulfonium nonaflate.

<u>Dissolution Inhibitors and Additives</u>

Various dissolution inhibitors can be utilized in this invention. Ideally, dissolution inhibitors (DIs) for far and extreme UV resists (e.g., 193 nm resists) should be designed/chosen to satisfy multiple materials needs including dissolution inhibition, plasma etch resistance, and

adhesion behavior of resist compositions comprising a given DI additive. Some dissolution inhibiting compounds also serve as plasticizers in resist compositions.

A variety of bile-salt esters (i.e., cholate esters) are particularly useful as DIs in the compositions of this invention. Bile-salt esters are known to be effective dissolution inhibitors for deep UV resists, beginning with work by Reichmanis et al. in 1983. (E. Reichmanis et al., "The Effect of Substituents on the Photosensitivity of 2-Nitrobenzyl Ester Deep UV Resists", *J. Electrochem. Soc.* 1983, 130, 1433-1437.) Bile-salt esters are particularly attractive choices as DIs for several reasons, including their availability from natural sources, their high alicyclic carbon content, and particularly for their transparency in the deep and vacuum UV region, (which essentially is also the far and extreme UV region), of the electromagnetic spectrum. Typically, they are highly transparent at 193 nm. Furthermore, the bile-salt esters are also attractive DI choices since they may be designed to have widely ranging hydrophobic to hydrophilic compatibilities depending upon hydroxyl substitution and functionalization.

Representative bile-acids and bile-acid derivatives that are suitable as additives and/or dissolution inhibitors for this invention include, but are not limited to cholic acid, deoxycholic acid, lithocholic acid, t-butyl deoxycholate, t-butyl lithocholate, and t-butyl-3-α-acetyl lithocholate.

The invention is not limited to use of bile-acid esters and related compounds as dissolution inhibitors. Other types of dissolution inhibitors, such as various diazonaphthoquinones (DNQs) and diazocoumarins(DCs), can be utilized in this invention in some applications. Diazanaphthoquinones and diazocoumarins are generally suitable in resists compositions designed for imaging at higher wavelengths of UV light (e.g., 365 nm and perhaps at 248 nm). These dissolution inhibitors are generally not preferred in resist compositions designed for imaging with UV light at 193 nm or lower wavelengths, since these compounds absorb strongly in this region of the UV and are usually not sufficiently transparent for most applications at these low UV wavelengths.

The photoresist compositions of this invention can contain optional additional components together with the binder and the photoactive agent. Examples of additional components which can be added include, but are not limited to, one or more of resolution enhancers, adhesion promoters, crosslinking agents, residue reducers, coating aids, plasticizers, solvents

and T_g (glass transition temperature) modifiers. Suitable solvents are typically organic such as 2-heptanone, propylene glycol methyl ether acetate and trichlorobenzene.

Solvents

Photoresists of this invention are prepared as coating compositions by dissolving the components of the photoresist in a suitable solvent, for example, ether esters such as propyleneglycol monomethyl ether acetate, 2-ethoxyethyl acetate, 2-methoxyethyl acetate, and ethyl 3-ethoxypropionate; ketones such as cyclohexanone, 2-heptanone, and methyl ethyl ketone; esters such as butyl acetate, ethyl lactate, methyl lactate, and ethyl acetate; glycol ethers such as propylene glycol monomethyl ether, ethylene glycol monomethyl ether, ethyleneglycol monoethyl ether, and 2-methoxyethyl ether (diglyme); unsubstituted and substituted hydrocarbons and aromatic hydrocarbons such as hexane, toluene, and chlorobenzene; and fluorinated solvents such as CFC-113 (1,1,2-trichlorotrifluoromethane, E. I. du Pont de Nemours and Company), and 1,2-bis(1,1,2,2-tetrafluoroethoxy)ethane. High boiling solvents can be added, for example, xylene or other unsubstituted or substituted aromatic hydrocarbons; ethers such as benzyl ethyl ether, and dihexyl ether; glycol ethers such as diethyleneglycol monomethyl ether, and diethyleneglycol monoethyl ether; ketones such as acetonylacetone, and isophorone; alcohols such as 1-octanol, 1-nonanol, and benzylalcohol; esters such as benzyl acetate, ethyl benzoate, diethyl oxalate, diethyl maleate, ethylene carbonate, and propylene carbonate; and lactones such as γ-butyrolactone and δ-valerolactone. Alternatively, supercritical CO_2 may be useful as a solvent. These solvents may be used alone or in admixture of two or more. Typically, the solids content of the photoresist varies between 5 and 50 percent by weight of the total weight of the photoresist composition.

Imagewise Exposure

The photoresist compositions of this invention are sensitive in the ultraviolet region of the electromagnetic spectrum and especially to those wavelengths greater than or equal to 365 nm. Imagewise exposure of the resist compositions of this invention can be done at many different UV wavelengths including, but not limited to, 365 nm, 248 nm, 193 nm, 157 nm, and lower wavelengths. Imagewise exposure is preferably done with ultraviolet light of 248 nm, 193 nm, 157 nm, or lower wavelengths; is more preferably done with ultraviolet light of 193 nm, 157 nm, or lower wavelengths; and is still more preferably done with ultraviolet light of

157 nm or lower wavelengths. Imagewise exposure can either be done digitally with a laser or equivalent device or non-digitally with use of a photomask. Suitable laser devices for digital imaging of the compositions of this invention include, but are not limited to, an argon-fluorine excimer laser with UV output at 193 nm, a krypton-fluorine excimer laser with UV output at 248 nm, and a fluorine (F2) laser with output at 157 nm. Since, as discussed supra, use of UV light of lower wavelength for imagewise exposure corresponds to higher resolution (lower resolution limit), the use of a lower wavelength (e.g., 193 nm or 157 nm or lower) is generally preferred over use of a higher wavelength (e.g., 248 nm or higher).

Development

The photoresists derived from the polymers of this invention can either be positive- or negative-working photoresists, depending upon choice of components in the fluoropolymer, the presence or absence of optional dissolution inhibitor and crosslinking agents, and the choice of solvent used in development.

In positive-working photoresists, the polymer becomes more soluble and/or dispersible in a solvent used in development in the imaged or irradiated areas whereas in a negative-working photoresist, the polymer becomes less soluble and/or dispersible in the imaged or irradiated areas. In one preferred embodiment of this invention, irradiation causes the generation of acid or base by the photoactive component. The acid or base may catalyze removal of protecting groups from the polymer, for example from the fluoroalcohol or other acidic groups present in the polymer.

Development in an aqueous base such a tetramethylammonium hydroxide would result in the formation of a positive image whereas development in an organic solvent or critical fluid (having moderate to low polarity), would result in a negative-working system in which exposed areas remain and unexposed areas are removed. Positive-working photoresists are preferred.

A variety of different crosslinking agents can be employed in the photoresist composition as required or optional photoactive component(s) in the negative-working mode of this invention. (A crosslinking agent is required in embodiments that involve insolubilization in developer solution as a result of crosslinking, but is optional in preferred embodiments that involve insolubilization in developer solution as a result of polar groups being formed in exposed areas that are insoluble in organic solvents and

critical fluids having moderate/low polarity). Suitable crosslinking agents include, but are not limited to, various bis-azides, such as 4,4'-diazidodiphenyl sulfide and 3,3'-diazidodiphenyl sulfone. Preferably, a negative-working resist composition containing a crosslinking agent(s) also contains suitable functionality (e.g., unsaturated C=C bonds) that can react with the reactive species (e.g., nitrenes) that are generated upon exposure to UV to produce crosslinked polymers that are not soluble, dispersed, or substantially swollen in developer solution, which consequently imparts negative-working characteristics to the composition.

The fluorine-containing polymers of this invention when used as the binder of a resist composition must contain sufficient functionality for development following imagewise exposure to UV light. Preferably, the functionality is acid or protected acid such that aqueous development is possible using a basic developer such as sodium hydroxide solution, potassium hydroxide solution, or ammonium hydroxide solution. Typically, the level of acidic groups, typically furnished by an acidic fluoralcohol, can be determined for a given composition by optimizing the amount needed for good development in aqueous alkaline developer.

When an aqueous processable photoresist is coated or otherwise applied to a substrate and imagewise exposed to UV light, development of the photoresist composition may require that the polymer used as the binder component contain sufficient acidic groups (e.g., fluoroalcohol groups) and/or protected acidic groups that are at least partially deprotected upon exposure to render the photoresist (or other photoimageable coating composition) processable in aqueous alkaline developer. In case of a positive-working photoresist layer, the photoresist layer will be removed during development in portions which are exposed to UV radiation but will be substantially unaffected in unexposed portions during development by aqueous alkaline liquids such as wholly aqueous solutions containing 0.262 N tetramethylammonium hydroxide (with development at 25°C usually for less than or equal to 120 seconds). In case of a negative-working photoresist layer, the photoresist layer will be removed during development in portions which are unexposed to UV radiation but will be substantially unaffected in exposed portions during development using either a critical fluid or an organic solvent.

A critical fluid, as used herein, is one or more substances heated to a temperature near or above its critical temperature and compressed to a pressure near or above its critical pressure. Critical fluids in this invention

are at least at a temperature that is higher than 15°C below the critical temperature of the fluid and are at least at a pressure higher than 5 atmospheres below the critical pressure of the fluid. Carbon dioxide may be used for the critical fluid in the present invention. Various organic solvents can also be used as developer in this invention. These include, but are not limited to, halogenated solvents and non-halogenated solvents. Halogenated solvents are preferred and fluorinated solvents are more preferred.

The substrate employed in this invention can illustratively be silicon, silicon oxide, silicon nitride, or various other materials used in semiconductive manufacture.

In a further embodiment of the invention is provided an article comprising a semi-conducting substrate having a surface, and a photoresist film disposed upon at least a portion of said surface, said photoresist film comprising a photoactive group and a polymer as described herein.

Preferably said semi-conducting substrate is silicon. The photoresist film disposed thereupon may be so disposed by any convenient method. Spin-coating a solution is a particularly attractive method for casting thin uniform polymeric films upon a substrate. The photoresist film thickness is typically in the range of about 50 nm to about 500 nm.

In a further embodiment of the present invention is provided a process for preparing a patterned article by photolithography, the process comprising:

forming a target surface by disposing upon a semiconducting substrate a photoresist film comprising a photoactive group and a polymer as described hereinabove, forming a pattern of shadowed and illuminated areas on a target surface by illuminating the target surface followed by an optional heating step, said illuminating and optional heating being sufficient to change the solubility of said polymer;

forming a patterned article by removing the soluble portions of said polymer, thereby producing a patterned article.

Preferably the target surface is illuminated by exposure to a light source. The light source can be in the vacuum ultra-violet, having a wavelength range of 140 nm to 260 nm. Most preferably the light is a source in the VUV having a wavelength in the range of 140 to 200 nm.

One of skill in the art will appreciate that once the patterned article of the invention is prepared according to the process hereof, or any alternative process such as is known in the art, additional processing steps may be conducted directed at the fabrication of an electronic circuit. Such additional processing steps may include chemical or ion-beam etching, metallization, doping and other processes known in the art, and combinations thereof.

The present invention is further described in the following examples.

Examples

Materials

$ICH_2C(CF_3)_2OH$ was prepared by the reaction of 47% hydroiodic acid with 2,2-bis(trifluoromethyl)oxirane (supplied by E. I. DuPont de Nemours and Company) according to the method in V.A.Petrov, *Synthesis*, 15, 2225, (2002). A mixture of endo-exo isomers of 5-chloronorbornene-2 was prepared by Diels-Alder reaction of vinyl chloride and dicyclopentadiene (supplied by Aldrich) at 180°C, for 12 h. Predominantly exo-5-chloronorbornene-2 was prepared by low temperature addition of HCl to norbornadiene according to the method of L. Schmerling, J.P. Luvisi, W. Welch, *JACS*, 78 (1956) 2819. Material prepared by this method contained 25% of nortricyclyl chloride and was used without purification. The inventors hereof believe that nortricyclyl chloride is not active under radical conditions.

Dry THF (supplied by Aldrich 99.9%, water 0.005%) and diglyme (supplied by Aldrich 99.9%, water 0.005%) and potassium t-butoxide (supplied by Aldrich, 95%), norbornadiene (supplied by Acros, 96%) were purchased from commercial sources and used without further purification.

GLOSSARY

Analytical/Measurements

bs	broad singlet
δ	NMR chemical shift measured in the indicated solvent
g	gram
h	hours
NMR	Nuclear Magnetic Resonance
^{1}H NMR	Proton NMR
^{13}C NMR	Carbon-13 NMR
^{19}F NMR	Fluorine-19 NMR

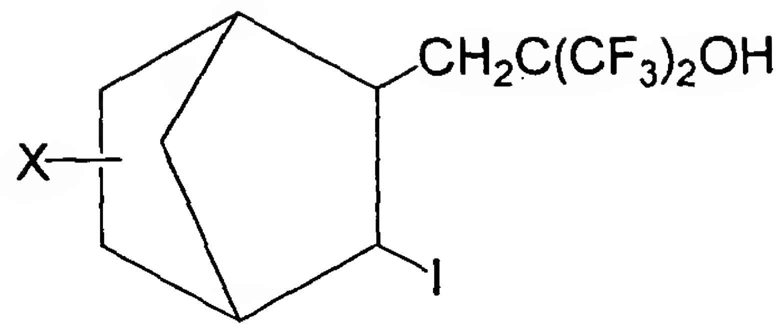
s	singlet
sec.	second(s)
m	multiplet
mL	milliliter(s)
mm	millimeter(s)
T_g	Glass Transition Temperature
M_n	Number-average molecular weight of a given polymer
M_w	Weight-average molecular weight of a given polymer
$P = M_w/M_n$	Polydispersity of a given polymer
Absorption coefficient	AC = A/b, where A, absorbance, = $Log_{10}(1/T)$ and b = film thickness in microns, where T = transmittance as defined below.

Transmittance Transmittance, T, = ratio of the radiant power transmitted by a sample to the radiant power incident on the sample and is measured for a specified wavelength λ (e.g., nm).

Example 1: Preparation of Composition IV-A

13 g (0.1 mol) of a mixture endo- and exo-5-chloronorbornene-2 with an endo/exo ratio of 73/27 was combined at ambient temperature with 35 g (0.11 mol) of $ICH_2C(CF_3)_2OH$ to which combination was added 1.5 g of 2,2'-azobis(2-methyl)propionitrile (AIBN, supplied by Aldrich, 98%) initiator. The reaction mixture was agitated at 70-80°C under nitrogen atmosphere for 3 hours.

The reaction mixture was cooled to ambient temperature and an additional 1.5 g of AIBN was added. Heating was continued for another 3 hours and the reaction mixture was agitated for 10 hours at ambient temperature. The reaction mixture was washed with 200 mL of water, dried over $MgSO_4$ and distilled under vacuum to give 9 g (yield 21%) of product **IV-A** (mixture of isomers), b.p. 90-96/0.11 mm and 25 g of higher boiling point residue.



IV-A

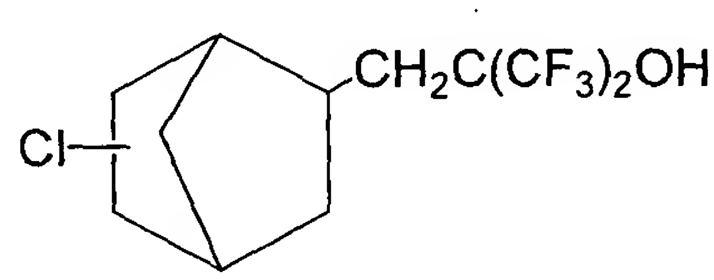
Wherein X is chlorine.

Example 2. Reduction of Composition IV-A

Example 2a: Reduction of Composition IV-A using Zinc

58 g of the composition (IV-A) so prepared but not distilled, was dissolved in 150 mL of ethanol (96%); the solution was added to a 3-neck flask containing 26 g of Zn dust (supplied by Acros, 97%) and equipped with water condenser, thermometer and addition funnel. The mixture was preheated to 40°C under agitation. Hydroiodic acid (50 mL, 47 wt. %) was added slowly from an addition funnel over a period of ca. 1 hour. During addition the temperature quickly rose to 60°C. The rate of the acid addition was adjusted to maintain internal temperature of the reaction mixture at 60-70°C.

The reaction mixture was maintained at 60°C for an additional hour. The liquid part of the reaction mixture was decanted and the solid residue was washed with two 50 mL aliquots of ethanol. The combined ethanolic wash solutions were diluted with 1 L of water; 100 mL of CH_2Cl_2 was added; the organic layer formed thereby was separated, water was extracted with two 50 mL aliquots of CH_2Cl_2 The combined CH_2Cl_2 wash solutions were dried over $MgSO_4$, filtered, the solvent was removed under vacuum and the residue distilled under vacuum to give 18 g (45 %) of the mixture of isomers represented by structure VII, b.p. 58-64/0.1 mm. The product was a liquid.



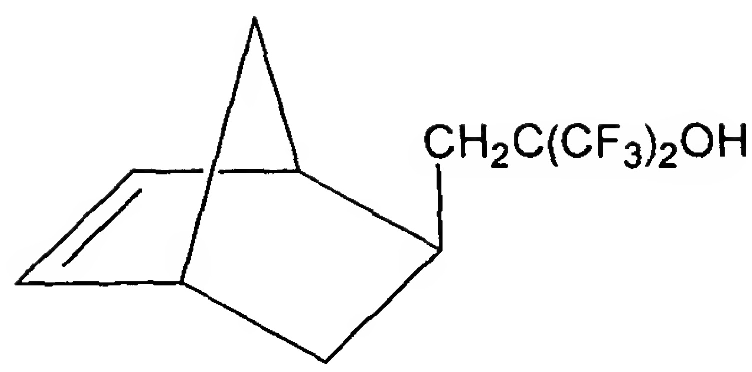
VII

Example 2b: Reduction of Composition IV-A using Hydrogen

40 g of the purified compound represented by structure (IV-A) prepared in Example 1 was combined with 150 mL of ethanol, 20 g of K_2CO_3, and 1 g of palladium on carbon (5%, supplied by Aldrich). The mixture so prepared was agitated at 50°C under constant 400 psi pressure of hydrogen for 12 hours. The reaction mixture was filtered through Celite^R 545 (supplied by Spectrum Chem. Corp.), diluted with 500 mL of 10 % hydrochloric acid, and water was extracted with three 70 mL aliquots of CH_2Cl_2. The three aliquots were combined, the solution was dried to extract any remaining water. Solvent was removed under vacuum to leave 20 g (yield 69%) of material represented by the structure (VII)(96% purity, contained 4% of CH_2Cl_2; NMR).

Example 3: Preparation of Compound VIII

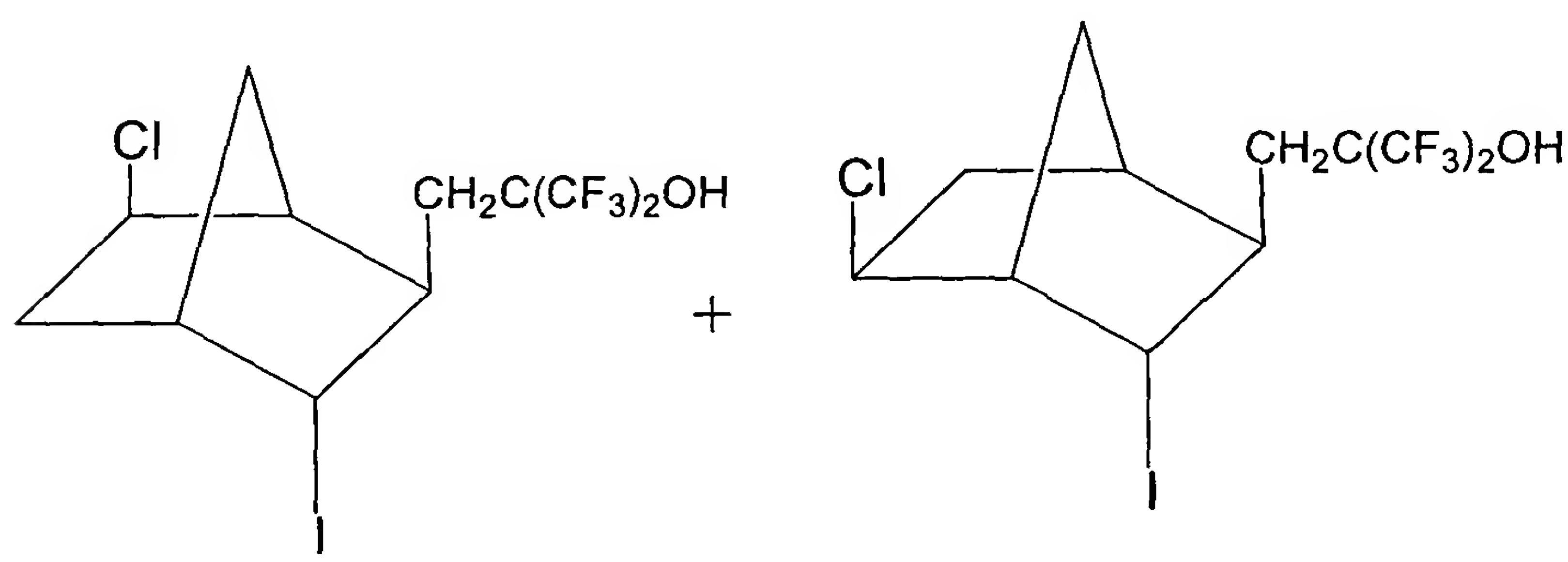
A 250-ml glass flask was charged with 32 g (0.28 mol) of potassium t-butoxide inside of a dry box with a nitrogen atmosphere. 150 mL of dry diglyme was added and mixture was agitated until all solids dissolved A solution of 18 g (0.058 mol) compound VII in 50 mL of dry diglyme was added slowly to the solution of potassium t-butoxide to maintain internal temperature of the reaction mixture < 40°C. The reaction mixture was heated to 100°C and held at that temperature for 9 hours under agitation. The reaction mixture was brought to ambient temperature, diluted with 1 L of 10% hydrochloric acid, and extracted with three 100 mL aliquots of CH_2Cl_2. The product was poorly soluble in water. The precipitated organic layer was dissolved in the first aliquot of solvent; residual product was extracted from water by the additional amounts of solvent. The aliquots following extraction were combined, was dried over $MgSO_4$, and solvent was removed under vacuum. The liquid residue was distilled using a spinning band column to give 18.5 g of a fraction with a boiling point in the range of 60-62°C/at 0.6 mm, containing about 40% diglyme. This fraction was redistilled using spinning band column to give 6 g (yield 40%) of the compound represented by the structure (VII), indicating the exo isomer at 98% purity; the remainder was diglyme. The endo- isomer of VIII was not detected in the distilled product using either ^{19}F or ^{1}H NMR spectroscopy.



VIII

Example 4: Preparation of Composition IX

To a mixture of 17.15 g of exo-5-chloronorbornene-2 (75% purity, the rest was nortricyclyl chloride, 0.1 mol of exo-5-chloronorbornene-2) and 61.6 g (0.2 mol) of $ICH_2C(CF_3)_2OH$ was added 1.64 g of AIBN initiator and the reaction mixture was heated to 70-80°C for 9.5 hours under agitation. The combined crude reaction mixture from two separate runs was distilled under vacuum to give 181 g (yield 69% based on 0.6 mol reaction scale) of IX b.p. 87-102/0.3 mm.

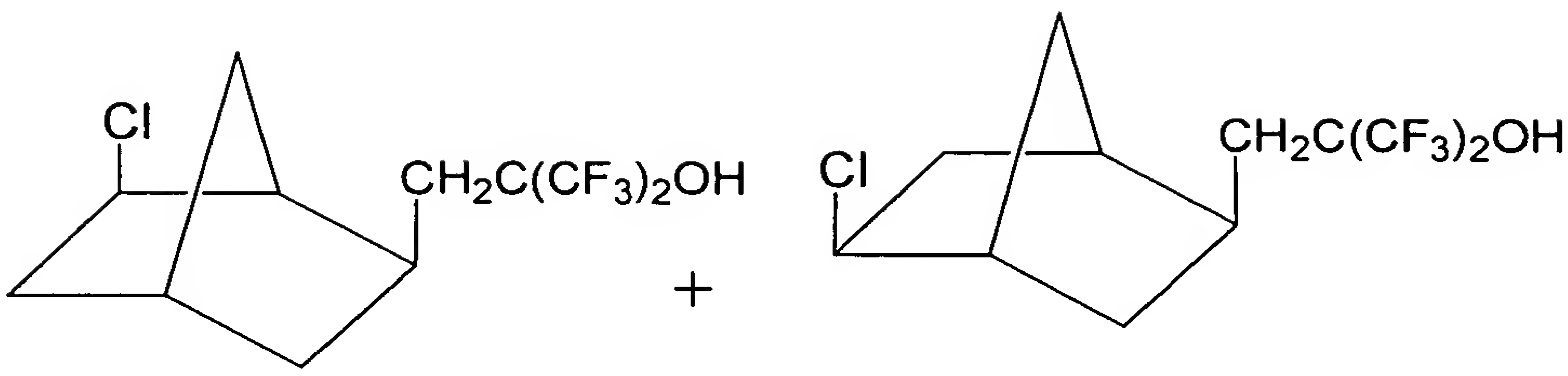


IX

Reduction of IX.

Example 5a: Reduction using Zinc

According to the procedure given in Example 2a, 68 g of IX was combined in 200 mL of ethanol (96%) with 31 g of Zn dust and 70 mL of hydroiodic acid. of the product represented by the structures (X) was isolated after distillation (15.5 g yield 32 %; b.p. 52-60 at 0.1 mm).



X

Example 5b: Reduction of IX using Hydrogen.

The purified iodide, IX, (82g) prepared in Example 4 was dissolved in 200 mL of ethanol, and the resulting solution added to a 400 mL shaker tube. To the tube was added 50 g of solid $NaHCO_3$ and 1g of palladium on carbon (5%, supplied by Aldrich). The reactor was cooled to –40°C, evacuated and charged with 400 psi of hydrogen and kept at 80°C for 2 hours, then further pressurized to 500 psi of hydrogen, kept at 80°C for 2 hours, then further pressurized to 900 psi of hydrogen and kept at 80°C for 10 hours. The reaction mixture was filtered through approximately 5 cm layer of Celite^R 545, diluted with 700 mL of water, and extracted with three 100 mL aliquots of CH_2Cl_2. The three 100 mL aliquots were then combined in a separate vessel and washed with two 300 mL aliquots of 0.1 molar solution of sodium thiosulfate and dried over $MgSO_4$. The solvent was removed under vacuum and the liquid residue (58 g) was distilled at 0.4 mm Hg to give 42 g (72%) of the product, X. b.p. 60-68°C at 0.4 mm. Found: C, 42.40, H, 4.21, F, 36.82. ^{1}H NMR (mixture isomers, $CDCl_3$): 1.1-2.1 (11H, m), 2.2-2.5 (2H), 2.7-2.8(1H), 3.9 (1H, m).^{19}F (mixture isomers, $CDCl_3$): -76.9 to –77.4 (3F, m), -77.5 to –77.9 (3F, m).

Example 6: Dehydrochlorination of X.

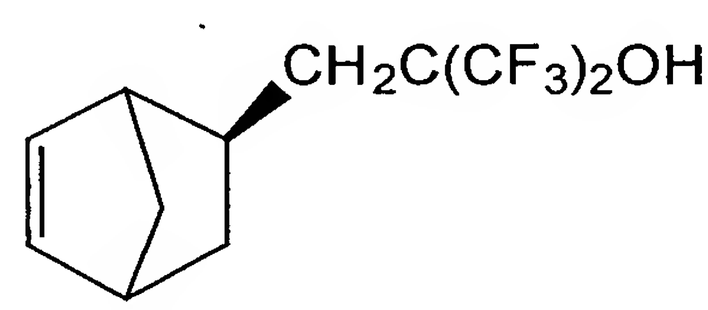
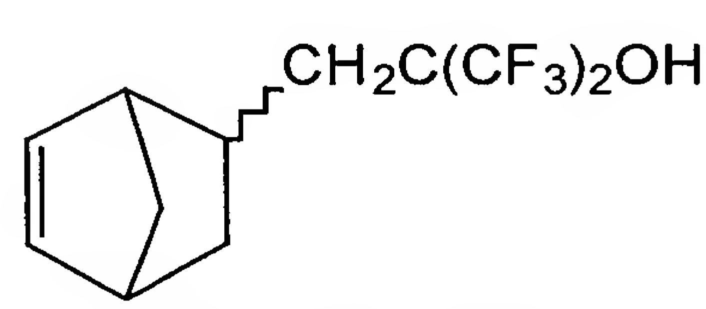
A 1 L round bottom flask was charged with 96 g (0.86 mol) of $KOC(CH_3)_3$ inside of a nitrogen filled glove box. The flask was fitted with a thermocouple, a reflux water condenser and an addition funnel. Dry THF (250 mL) was added to the flask and the mixture so formed was agitated for 5 min to dissolve most of the solids. A solution of 44 g of the product X in 50ml of dry THF was added dropwise over a period of 5 min. During the addition, the internal temperature rose to 45°C. The addition funnel was replaced with a glass stopper and the reaction mixture was refluxed at 69-70°C for 15h. Gas chromatography indicated that the conversion of X after 15 hours was >98%.

The solvent was removed under vacuum of approximately 100 to 1 mm, and the solid residue was dissolved in 700 mL of water and about 70 ml of concentrated hydrochloric acid was slowly added to the solution at 10-20°C to achieve a pH ≈ 1). The reaction mixture was extracted with two 100 mL aliquots of CH_2Cl_2. The organic layers from the two aliquots were combined, washed with two 300 mL aliquots of 10% HCl, and dried over $MgSO_4$. The solvent was removed under vacuum to give 54 g of crude product. Combined crude product, total weight of 116 g, from two consecutive runs (scale 0.14 mol and 0.18 mol respectively) was distilled under vacuum using a spinning band column to give 80 g (91%) of (VIII), b.p. 84-84.7°C /17mm, containing <3 % of endo isomer (NMR; GC). Found: C, 47.52, H, 4.40, F, 41.59.

^{1}H NMR ($CDCl_3$): 1.4(4H,m), 1.7 (1H, s), 2.1(2H, m), 2.6(1H, s), 2.7(1H, s), 2.8(1H, s), 6.14 (2H, m). ^{19}F NMR ($CDCl_3$): -77.4 (6F, m) ^{13}C NMR {H}(neat): 32.2(s); 34.5(s), 36.7(s), 42.2 (s), 35.0 (s), 48.4 (s), 76.9 (hept, 28 Hz), 123.3 (q, 287 Hz), 136.4 (s), 136.8 (s).

Examples 7-9 and Comparative Example A

The following glossary of terms pertains to the following examples.

HAdA	Hydroxyadamantyl acrylate OHKA America, Milpitas, CA
HFPO-dp	$[CF_3CF_2CF_2OCF(CF_3)CO_2]_2$. Prepared as described by Chengxue et. al., Journal of Organic Chemistry, vol 47, pages 2009 – 2013 (1982)
Exo-NB-CH_2-F-OH	 (exo-rich)
Endo/Exo-NB-CH_2-F-OH	 (high endo ratio)

Perkadox® 16 N	Di-(4-tert-butylcyclohexyl)peroxydicarbonate Noury Chemical Corp., Burt, NY
PinAc	2-Propenoic acid, 2-hydroxy-1,1,2-trimethylpropyl ester [CAS Reg number 97325-36-5]
Solkane 365 mfc	1,1,1,3,3-Pentafluorobutane Solvay Fluor, Hannover, Germany
t-BuAc	tert-Butyl acrylate Aldrich Chemical Company, Milwaukee, WI
TFE	Tetrafluoroethylene E. I. du Pont de Nemours and Company, Wilmington, DE
THF	Tetrahydrofuran Aldrich Chemical Co., Milwaukee, WI

EXAMPLE 7

Synthesis of a TFE, exo-NB-CH_2-F-OH, t-BuAc terpolymer

A metal pressure vessel of approximate 270 mL capacity was charged with 67.12 g exo-NB-CH_2-F-OH prepared as described in Example 6, 0.64 g tert-butyl acrylate and 25 mL Solkane 365 mfc. The vessel was closed, cooled to about -15°C, and pressurized to 400 psi with nitrogen and vented several times. The reactor contents at about atmospheric pressure were heated to 50°C. TFE was added to a total pressure of 340 psi and a pressure regulator was set to maintain the pressure at 340 psi throughout the polymerization by adding TFE as required. A monomer feed solution (100mL) was prepared by combining 78.01 g of the exo-NB-CH_2-F-OH and 8.00 g of tert-butyl acrylate in Solkane 365 mfc. The solution so prepared was pumped into the reactor at a rate of 0.10 mL/minute for 12 hours. Simultaneously, a solution of 7.3 g Perkadox®16N and 60 mL methyl acetate diluted to 100 mL with Solkane 365 mfc was pumped into the reactor at a rate of 2.0 mL/minute for 6 minutes, and then at a rate of 0.1 mL/minute for 8 hours. After 16 hours of reaction, the vessel was cooled to room temperature and vented to 1 atmosphere. The recovered polymer solution was added slowly while stirring to an excess of hexane to precipitate the polymer. Hexane is a non-solvent for the polymer. The precipitate formed thereby was filtered, washed with hexane and air dried. The resulting solid was dissolved in a mixture of THF and Solkane 365 mfc and added slowly to

excess hexane. The precipitate so formed was filtered, washed with hexane and dried in a vacuum oven overnight to give 19.7 g of white polymer. From its ^{13}C NMR spectrum, the polymer composition was found to be 36% TFE, 50% *exo*-NB-CH2-F-OH and 14% t-BuAc. DSC: Tg = 154°C. GPC: Mn = 5800; Mw = 7500; Mw/Mn = 1.29. Anal. Found: C, 46.11; H, 4.08; F, 41.75.

COMPARATIVE EXAMPLE A

Synthesis of a TFE, endo/exo NB-CH_2-F-OH, t-BuAc terpolymer

The procedure in Example 7 was followed except that an endo/exo-NB-CH_2-F-OH mixture, prepared as described by Ito et al, US 2002/0102490 was used in place of the exo-NB-CH_2-F-OH of Example 6. Isolated was 8.5 g of white polymer. From its ^{13}C NMR spectrum, the polymer composition was found to be 24% TFE, 47% endo/exo-NB-CH_2-F-OH and 29% t-BuAc. DSC: Tg = 166°C. GPC: Mn = 5800; Mw = 7000; Mw/Mn = 1.20. Anal. Found: C, 49.03; H, 4.87; F, 36.90.

EXAMPLE 8

Synthesis of a TFE, exo-NB-CH_2-F-OH, t-butyl acrylate terpolymer

A metal pressure vessel of approximate 270 mL capacity was charged with 67.12 g exo-NB-CH_2-F-OH, 0.64 g tert-butyl acrylate and 25 mL Solkane 365. The vessel was closed, cooled to about -15 °C and pressured to 400 psi with nitrogen and vented several times. The reactor contents were heated to 40°C. TFE was added to a pressure of 340 psi and a pressure regulator was set to maintain the pressure at 340 psi throughout the polymerization by adding TFE as required. A solution of 78.01 g of *exo*-NB-CH_2-F-OH and 8.00 g of tert-butyl acrylate diluted to 100 mL with Solkane 365 mfc was pumped into the reactor at a rate of 0.10 mL/minute for 12 hours. Simultaneously with the monomer feed solution, a 0.28 molar solution of HFPO-dp in Solkane 365 mfc was pumped into the reactor at a rate of 2.0 mL/minute for 6 minutes, and then at a rate of 0.1 mL/minute for 8 hours. After a 16 hours reaction time, the vessel was cooled to room temperature and vented to 1 atmosphere. The recovered polymer solution was added slowly to an excess of hexane while stirring. The precipitate was filtered, washed with hexane and air dried. The resulting solid was dissolved in a mixture of THF and Solkane 365 mfc and added slowly to excess to hexane. The precipitate was filtered, washed with hexane and dried in a vacuum oven overnight to give 29.5 g of white polymer. From its ^{13}C NMR spectrum, the polymer

composition was found to be 41% TFE, 47% exo-NB-CH_2-F-OH and 11 % t-BuAc. DSC: Tg = 145 °C. GPC: Mn = 6200; Mw = 8100; Mw/Mn = 1.31. Anal. Found: C, 43.22; H, 3.42; F, 43.38.

EXAMPLE 9

Synthesis of a TFE, exo-NB-CH_2-F-OH, PinAc, and HAdA tetrapolymer

A metal pressure vessel of approximate 270 mL capacity was charged with 72.34 g *exo*-NB-CH_2-F-OH, 3.72 g PinAc, 3.20 g HAdA and 35 mL Solkane 365. The vessel was closed, cooled to about -15°C and pressured to 400 psi with nitrogen and vented several times. The reactor contents were heated to 50°C. TFE was added to a pressure of 270 psi and a pressure regulator was set to maintain the pressure at 270 psi throughout the polymerization by adding TFE as required. A solution of 47.95 g of exo-NB-CH_2-F-OH, 25.08 g PinAc and 21.28 g HAdA diluted to 100 mL with Solkane 365 mfc was pumped into the reactor at a rate of 0.10 mL/minute for 12 hours. Simultaneously with the monomer feed solution, a solution of 7.3 g Perkadox®16N and 60 mL methyl acetate diluted to 100 mL with Solkane 365 mfc was pumped into the reactor at a rate of 2.0 mL/minute for 6 minutes, and then at a rate of 0.1 mL/minute for 8 hours. After a 16 hours reaction time, the vessel was cooled to room temperature and vented to 1 atmosphere. The recovered polymer solution was added slowly to an excess of hexane while stirring. The precipitate was filtered, washed with hexane and air dried. The resulting solid was dissolved in a mixture of THF and Solkane 365 mfc and added slowly to excess to hexane. The precipitate was filtered, washed with hexane and dried in a vacuum oven overnight to give 80.1 g of white polymer. From its ^{13}C NMR spectrum, the polymer composition was found to be 9% TFE, 41% exo-NB-CH_2-F-OH, 32% PinAc and 18% HAdA. GPC: Mn = 7500; Mw = 14400; Mw/Mn = 1.93. Anal. Found: C, 54.86; H, 6.10; F, 24.58.

EXAMPLE 10

A coating solution of the following composition was prepared and magnetically stirred overnight.

Component	Wt. (gm)
TFE/exo-NB-CH_2-F-OH/PinAc/HAdA polymer in Example 9	1.140
2-Heptanone	7.980
6.82% (wt) solution of triphenylsulfonium nonaflate (Midori Kagaku Co, Ltd.) dissolved in 2-heptanone which had been filtered through a 0.45μ PTFE syringe filter.	0.880

A 4 inch diameter Type "P", <100> orientation, silicon wafer was prepared by applying an hexamethyldisilazane (HMDS) prime layer using a YES-3 vapor prime oven. A 100% HMDS adhesion promoter from Arch Chemical Co. was used. The oven was programmed to give a 5 minute prime at 150 – 300°C.

2 mL of the above prepared coating solution was filtered through a 0.45 micrometer poly-tetrafluoroethylene (PTFE) syringe filter (Whatman Filters Co.) and deposited onto the thus prepared wafer. Spin-coating was accomplished employing a Brewer Science Inc. Model-100CB combination spin coater/hotplate. The wafer was spun at 2500 rpm for 60 seconds and then baked at 120°C for 60 seconds.

248 nm imaging was accomplished by exposing the thus prepared coated wafer to light obtained by passing broadband UV light from an ORIEL Model-82421 Solar Simulator (1000 watt) through a 248 nm interference filter which passes about 30% of the energy at 248 nm. Exposure time was 30 seconds, providing an unattenuated dose of 45 mJ/cm^2. By using a mask with 18 positions of varying neutral optical density, a wide variety of exposure doses were generated. After exposure the exposed wafer was baked at 120°C for 60 seconds.

The wafer was tray-developed for 60 sec in aqueous tetramethylammonium hydroxide (TMAH) solution (Shipley LDD-026w, 2.38% TMAH solution). A positive image was obtained with a clearing dose of ≈ 20 mJ/cm^2.

EXAMPLE 11

A coating solution of the following composition was prepared and magnetically stirred overnight.

Component	Wt. (gm)
TFE/exo-NB-CH_2-F-OH/PinAc/HAdA polymer in Example 9	1.020
2-Heptanone	7.980
t-Butyl Lithocholate	0.120
6.82% (wt) solution of triphenylsulfonium nonaflate dissolved in 2-heptanone which had been filtered through a 0.45μ PTFE syringe filter.	0.880

The wafer was prepared and processed as in Example 10. A positive image was obtained with a clearing dose of ≈ 9.7 mJ/cm^2.

EXAMPLE 12

A coating solution of the following composition was prepared and magnetically stirred overnight.

Component	Wt. (gm)
TFE/exo-NB-CH_2-F-OH/tBA polymer in Example 8	0.798
2-Heptanone	5.586
6.82% (wt) solution of triphenylsulfonium nonaflate dissolved in 2-heptanone which had been filtered through a 0.45μ PTFE syringe filter.	0.616

The wafer was prepared and processed as in Example 10. A positive image was obtained with a clearing dose of ≈ 4.4 mJ/cm^2.

EXAMPLE 13

A coating solution of the following composition was prepared and magnetically stirred overnight.

Component	Wt. (gm)
TFE/exo-NB-CH_2-F-OH/tBA polymer in Example 8	0.714
2-Heptanone	5.586
t-Butyl Lithocholate	0.084
6.82% (wt) solution of triphenylsulfonium nonaflate dissolved in 2-heptanone which had been filtered through a 0.45μ PTFE syringe filter.	0.616

The wafer was prepared and processed as in Example 10. A positive image was obtained with a clearing dose of ≈ 9.7 mJ/cm^2.

The description of illustrative and preferred embodiments of the present invention is not intended to limit the scope of the invention. Various modifications, alternative constructions and equivalents may be employed without departing from the true spirit and scope of the appended claims.